## CERTIFICATE OF TRANSLATION

I, the undersigned, Konomi MACHIDA, residing at 6-181, Koyodai 3-chome, Kawanishi-shi, Hyogo 666-0115, Japan state that the attached document is a true and complete translation to the best of my knowledge of Japanese Patent Application No. 2002-361701.

Dated this 16th day of June, 2006

Signature of translator:

Konomi MACHIDA

# PATENT OFFICE JAPANESE GOVERNMENT

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[Title of the Invention]

Alloy Type Thermal Fuse and Material for a Thermal 5 Fuse Element

[Scope of the Claims]

[Claim 1]

A material for a thermal fuse element wherein said material has an alloy composition in which In is 15% or larger and smaller than 37%, Sn is 5% or larger and 28% or smaller, and balance Bi, and in which, with respect to each of reference points of ternary Bi-In-Sn eutectic points of 57.5%Bi-25.2%In-17.3%Sn and 54.0%Bi-29.7%In-16.3%Sn, a range of ±2%Bi, ±1%In, and ±1%Sn is excluded.

#### 15 [Claim 2]

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A material for a thermal fuse element wherein 0.1 to 3.5 weight parts of one, or two or more elements selected from the group consisting of Ag, Au, Cu, Ni, Pd, Pt, Sb, Ga, and Ge are added to 100 weight parts of an alloy composition of claim 1.

[Claim 3]

An alloy type thermal fuse wherein a material for a thermal fuse element of claim 1 or 2 is used as a fuse element.

25 [Claim 4]

An alloy type thermal fuse according to claim 3, wherein said fuse element contains inevitable impurities.

[Claim 5]

An alloy type thermal fuse according to claim 3 or 4, wherein said fuse element is connected between lead conductors, and at least a portion of each of said lead conductors which is bonded to said fuse element is covered with a Sn or Ag film.

## [Claim 6]

An alloy type thermal fuse according to claim 3 or 4, wherein a pair of film electrodes are formed on a substrate by printing conductive paste containing metal particles and a binder, said fuse element is connected between said film electrodes, and said metal particles are made of a material selected from the group consisting of Ag, Ag-Pd, Ag-Pt, Au, Ni, and Cu.

## [Claim 7]

An alloy type thermal fuse according to any one of claims 3 to 6, wherein a heating element for fusing off said fuse element is additionally disposed.

#### [Claim 8]

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An alloy type thermal fuse according to any one of claims 3 to 6, wherein said fuse element connected between a pair of lead conductors is sandwiched between insulating films.

[Claim 9]

An alloy type thermal fuse according to any one of claims 3 to 6, wherein a pair of lead conductors are partly exposed from one face of an insulating plate to another face, said fuse element is connected to said lead conductor exposed portions, and said other face of said insulating plate is covered with an insulating material.

[Claim 10]

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An alloy type thermal fuse according to any one of claims 3 to 5, wherein lead conductors are bonded to ends of said fuse element, respectively, a flux is applied to said fuse element, said flux-applied fuse element is passed through a cylindrical case, gaps between ends of said cylindrical case and said lead conductors are sealingly closed, ends of said lead conductors have a disk-like shape, and ends of said fuse element are bonded to front faces of said disks.

[Detailed Description of the Invention]

20 [0001]

[Field of the Invention]

The present invention relates to a material for a Bi-In-Sn alloy type thermal fuse in which the operating temperature belongs to a range of 75 to 120°C, and also to such a thermal type fuse element.

[0002]

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[Prior Art]

An alloy type thermal fuse is widely used as a thermoprotector for an electrical appliance, a circuit element, or the like.

Such an alloy type thermal fuse has a configuration in which an alloy of a predetermined melting point is used as a fuse element, the fuse element is bonded between a pair of lead conductors, a flux is applied to the fuse element, and the flux-applied fuse element is sealed by an insulator.

The alloy type thermal fuse has the following operation mechanism.

The alloy type thermal fuse is disposed so as to thermally contact an electrical appliance or a circuit element which is to be protected. When the electrical appliance or the circuit element is caused to generate heat by any abnormality, the fuse element alloy of the thermal fuse is melted by the generated heat, and the molten alloy is divided and spheroidized because of the wettability with respect to the lead conductors or electrodes under the coexistence with the activated flux that has already melted. The power supply is finally interrupted as a result of advancement of the spheroid division. The temperature of the appliance is lowered by the power supply interruption, and

the divided molten alloys are solidified, whereby the nonreturn cut-off operation is completed.

[0003]

Conventionally, a technique in which an alloy composition having a narrow solid-liquid coexisting region between the solidus and liquidus temperatures, and ideally a eutectic composition is used as such a fuse element is usually employed, so that the fuse element is fused off at approximately the liquidus temperature (in a eutectic composition, the solidus temperature is equal to the liquidus tempera-10 In a fuse element having an alloy composition in which there is a solid-liquid coexisting region, namely, there is the possibility that the fuse element is fused off at an uncertain temperature in the solid-liquid coexisting 15 When an alloy composition has a wide solid-liquid coexisting region, the uncertain temperature width in which a fuse element is fused off in the solid-liquid coexisting region becomes large, and the operating temperature is In order to reduce the dispersion, largely dispersed. therefore, the technique in which an alloy composition hav-20 ing a narrow solid-liquid coexisting region between the solidus and liquidus temperatures, or ideally a eutectic composition is used is usually employed.

[0004]

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In a high-energy density secondary battery which is

generally used as a power source of a portable telephone, a notebook personal computer, or a like portable electronic apparatus, such as a lithium-ion battery or a lithium polymer battery, a large amount of heat is generated in an abnormal state. Therefore, a thermal fuse is attached to a battery pack, and, when a battery reaches a dangerous temperature, the thermal fuse operates to prevent abnormal heat generation from occurring. The operating temperature of such a thermal fuse is set to be within a range of 75 to 120°C.

[0005]

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Because of increased awareness of environment conservation, the trend to prohibit the use of materials harmful to a living body is recently growing, and also an element for such a thermal fuse is strongly requested not to contain a harmful element (Pb, Cd, Hg, Tl, etc.).

As an alloy composition which can satisfy the requirement, known is a Bi-In-Sn system. Conventionally, the following thermal fuses which have an alloy composition of Bi-In-Sn, and which satisfy the requirement of an operating temperature of 75 to 120°C are known: a thermal fuse in which a fuse element has an alloy composition of 47 to 49% Sn, 51 to 53% In, and an adequate amount of Bi, and which has an operating temperature of 105 to 115°C (Patent Reference Document 1); that in which a fuse element has an alloy

composition of 42 to 53% In, 40 to 46% Sn, and 7 to 12 % Bi, and which has an operating temperature of 95 to 105°C (Patent Reference Document 2); that in which a fuse element has an alloy composition of 51 to 53% In, 42 to 44% Sn, and 4 to 6% Bi, and which has an operating temperature of 107 5 to 113°C (Patent Reference Document 3); that in which a fuse element has an alloy composition of 1 to 15% Sn, 20 to 33% Bi, and the balance In, and which has an operating temperature of 75 to 100°C (Patent Reference Document 4); and that in which a fuse element has an alloy composition of 0.3 to 10 1.5% Sn, 51 to 54% In, and the balance Bi, and which has an operating temperature of 86 to 89°C (Patent Reference Document 5). Furthermore, a thermal fuse is known in which a fuse element has an alloy composition of a Bi-In system not containing Sn and of 45 to 55% Bi and the balance In, and 15 which has an operating temperature of 85 to 95°C (Patent Reference Document 6).

Moreover, an In-Sn eutectic alloy (52% In, 48% Sn) having a melting point of 119°C may be contemplated to be 20 used as a fuse element.

[0006]

[Patent Reference Document 1]

Japanese Patent Application Laying-Open No. 56-114237

[Patent Reference Document 2]

Japanese Patent Application Laying-Open No. 2001-266724
[Patent Reference Document 3]

Japanese Patent Application Laying-Open No. 59-8229
[Patent Reference Document 4]

Japanese Patent Application Laying-Open No. 2001-325867

[Patent Reference Document 5]

Japanese Patent Application Laying-Open No. 6-325670 [Patent Reference Document 6]

Japanese Patent Application Laying-Open No. 2002-150906

[0007]

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In view of increased power consumption and high capacity of a battery due to enhanced functions of an electrical appliance, and legislated product liability, also a thermal fuse is recently requested to exhibit, for example, aging resistance and heat cycle resistance for a long term, or to have high reliability. In the above-mentioned conventional art examples, In which is a highly reactive element is contained at a large amount or 50% or more. When the fuse element is subjected particularly to long-term aging, therefore, In in the surface of a fuse element reacts with a flux to produce an In salt, and the rate of incorporation into the flux is increased, so that the alloy composition of the fuse element is changed in the direction of reduction of In. As a result, the variation of the alloy composition shifts the operating temperature, or increases the

resistance of the fuse element, thereby causing reduction of the operating temperature due to self-heating. Furthermore, the function of the flux is reduced, and the operation characteristic of the thermal fuse is inevitably impaired. Therefore, the long-term aging resistance which is requested in a thermal fuse is hardly ensured.

The aging resistance is requested to be set so that the resistance of a fuse element is not largely changed or a thermal fuse does not malfunction even when no-load, rated-load, and humidified conditions are continued for a long term under an environment of a high temperature such as the holding temperature (which is the maximum holding temperature where the fuse does not operate even when a rated current that is obliged to be set by the safety standard is continued to be supplied for 168 hours, and which is usually set to a temperature that is lower than the operating temperature by 20°C). The conventional art examples hardly adapt to the long-term aging resistance.

[8000]

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As a Bi-In-Sn eutectic alloy which can satisfy the requirement of an operating temperature of 75 to 120°C, and in which the weight of In is considerably smaller than 50%, there are 79°C-eutectic (57.5% Bi, 25.2% In, and 17.3% Sn) and 81°C-eutectic (54.0% Bi, 29.7% In, and 16.3% Sn). In 79°C-eutectic, as apparent from Fig. 12 showing a result of

a differential scanning calorimetry analysis [which called a DSC, and in which a reference specimen (unchanged) and a measurement specimen are housed in an  $N_2$  gas-filled vessel, an electric power is supplied to a heater of the vessel to heat the samples at a constant rate, and a variation of the heat energy input amount due to a state change of the measurement specimen is detected by a differential thermocouple], however, solid phase transformation occurs in a temperature zone of about 52 to 58°C which is considerably lower than the melting point. In 81°C-eutectic, as apparent from Fig. 13 showing a result of a differential scanning calorimetry analysis, solid phase transformation occurs in a temperature zone of about 51 to 57°C which is considerably lower than the melting point. As a result of a thermal hysteresis straddling the transformation temperature zone, a fuse element receives repetitive distortion to produce the possibility that the operating temperature is lowered by an increased resistance or the fuse element is broken so as not to operate. Therefore, the long-term heat cycle characteristic which is requested in a thermal fuse is hardly ensured.

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The long-term heat cycle characteristic is requested to be set so that, even when a thermal fuse is subjected to a thermal hysteresis between a high temperature (usually, the above-mentioned holding temperature) which is lower

than the operating temperature and the room temperature or a below-freezing temperature (for example, -40°C), the resistance of a fuse element is not changed or a thermal fuse does not malfunction. However, the 79°C- and 81°C-eutectics hardly adapt to the long-term heat cycle resistance.

[0009]

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The melting characteristic of an alloy can be obtained by a DSC measurement. The inventor measured and eagerly studied DSCs of Bi-In-Sn alloys of various compositions, and found that, depending on the composition, the DSCs show melting characteristics of the patterns such as shown in (A) to (D) of Fig. 14, and, when a Bi-In-Sn alloy of the melt pattern of (A) of Fig. 14 is used as fuse elements, the fuse elements can be concentrically fused off in the vicinity of the maximum endothermic peak.

[0010]

The pattern of (A) of Fig. 14 will be described. the solidus temperature a, an alloy starts to be liquefied In accordance with progress of the liquidifica-(melted). tion, the absorption amount of heat energy is increased, and reaches the maximum at a peak p. After passing the point, the absorption amount of heat energy is gradually reduced, and becomes zero at the liquidus temperature b, thereby completing the liquidification. Thereafter, the temperature is raised in the state of the liquid phase. 25

The reason why a division operation of the fuse element occurs in the vicinity of the maximum endothermic peak p is estimated as follows. In a Bi-In-Sn composition showing such a melting characteristic, all constituting elements have excellent wettability so as to exhibit excellent wettability even in the solid-liquid coexisting region in the vicinity of the maximum endothermic peak p in which the liquid phase state has not yet been completely established. Therefore, spheroid division occurs before a state exceeding the solid-liquid coexisting region is attained.

[0011]

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In Fig. 14, (B) shows the melt pattern of a eutectic composition or a composition in the vicinity of the eutectic. In the pattern, the solid-liquid coexisting region is zero or very narrow.

[0012]

In the melt pattern of (C) of Fig. 14 among (C) and (D) of Fig. 14, the heat energy is slowly absorbed, and the wettability is not suddenly changed. Therefore, the point of a division operation of the fuse element is not determined in a narrow range. In the melt pattern of (D) of Fig. 14, there are plural endothermic peaks. At any one of the endothermic peaks, a division operation of the fuse element may probably occur. In both (C) and (D) of Fig. 14, therefore, the point of a division operation of the

fuse element cannot be concentrated into a narrow range. [0013]

From the result of the above consideration, the followings are effective for obtaining an environment adaptive alloy type thermal fuse in which an excellent operation characteristic can be ensured at an operating temperature of 75 to 120°C. Because of the unadaptability to the long-term heat cycle resistance, Bi-In-Sn eutectic alloys of 79°C-eutectic (57.5% Bi, 25.2% In, and 17.3% Sn), and 81°C-eutectic (54.0% Bi, 29.7% In, and 16.3% Sn), and those in the range adjacent to the compositions are excluded. Because of the long-term aging resistance, furthermore, the amount of In is restricted, the operating temperature of 75 to 120°C is satisfied, and the melt pattern fulfills that of (A) of Fig. 14 or approaches that of (B) of Fig. 14.

[0014]

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It is an object of the invention to, based on the consideration result, provide an alloy type thermal fuse of an operating temperature of 75 to 120°C in which a fuse element of a Bi-In-Sn alloy is used, which exhibits excellent heat cycle and aging resistances for a long term, and in which satisfactory operating characteristic can be ensured.

It is a further object of the invention to thin a fuse element to reduce the size and thickness of an alloy type thermal fuse.

[0015]

[Solution to the Problems]

The material for a thermal fuse element according to claim 1 has an alloy composition in which In is 15% or larger and smaller than 37%, Sn is 5% or larger and 28% or smaller, and balance Bi, and in which, with respect to each of reference points of ternary Bi-In-Sn eutectic points of 57.5%Bi-25.2%In-17.3%Sn and 54.0%Bi-29.7%In-16.3%Sn, a range of ±2%Bi, ±1%In, and ±1%Sn is excluded.

10 [0016]

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In the material for a thermal fuse element according to claim 2, 0.1 to 3.5 weight parts of one, or two or more elements selected from the group consisting of Ag, Au, Cu, Ni, Pd, Pt, Sb, Ga, and Ge are added to 100 weight parts of the alloy composition according to claim 1.

[0017]

The materials for a thermal fuse element are allowed to contain inevitable impurities which are produced in productions of metals of raw materials and also in melting and stirring of the raw materials, and which exist in an amount that does not substantially affect the characteristics. In the alloy type thermal fuses, a minute amount of a metal material or a metal film material of the lead conductors or the film electrodes is caused to inevitably migrate into the fuse element by solid phase diffusion, and, when the

characteristics are not substantially affected, allowed to exist as inevitable impurities.

[0018]

In the alloy type thermal fuse according to claim 3, 5 the material for a thermal fuse element according to claim 1 or 2 is used as a fuse element.

[0019]

The alloy type thermal fuse according to claim 4 is characterized in that, in the alloy type thermal fuse according to claim 3, the fuse element contains inevitable impurities.

[0020]

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The alloy type thermal fuse according to claim 5 is an alloy type thermal fuse in which, in the alloy type thermal fuse according to claim 3 or 4, the fuse element is connected between lead conductors, and at least a portion of each of the lead conductors which is bonded to the fuse element is covered with a Sn or Ag film.

[0021]

20 The alloy type thermal fuse according to claim 6 is an alloy type thermal fuse in which, in the alloy type thermal fuse according to claim 3 or 4, a pair of film electrodes are formed on a substrate by printing conductive paste containing metal particles and a binder, the fuse element is connected between the film electrodes, and the metal parti-

cles are made of a material selected from the group consisting of Ag, Ag-Pd, Ag-Pt, Au, Ni, and Cu.

[0022]

The alloy type thermal fuse according to claim 7 is an alloy type thermal fuse in which, in the alloy type thermal fuse of any one of claims 3 to 6, a heating element for fusing off the fuse element is additionally disposed.

[0023]

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The alloy type thermal fuse according to claim 8 is an alloy type thermal fuse in which, in the alloy type thermal fuse according to any one of claims 3 to 6, the fuse element connected between a pair of lead conductors is sandwiched between insulating films.

[0024]

The alloy type thermal fuse according to claim 9 is an alloy type thermal fuse in which, in the alloy type thermal fuse according to any one of claims 3 to 6, a pair of lead conductors are partly exposed from one face of an insulating plate to another face, the fuse element is connected to the lead conductor exposed portions, and the other face of the insulating plate is covered with an insulating material.

[0025]

The alloy type thermal fuse according to claim 10 is 25 an alloy type thermal fuse in which, in the alloy type

thermal fuse according to any one of claims 3 to 5, lead conductors are bonded to ends of the fuse element, respectively, a flux is applied to the fuse element, the flux-applied fuse element is passed through a cylindrical case, gaps between ends of the cylindrical case and the lead conductors are sealingly closed, ends of the lead conductors have a disk-like shape, and ends of the fuse element are bonded to front faces of the disks.

[0026]

## 10 [Embodiments]

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In the invention, a fuse element of a circular wire or a flat wire is used. The outer diameter or the thickness is set to 100 to 800  $\mu m$ , preferably, 300 to 600  $\mu m$ .

[0027]

The reasons why, in claim 1, a thermal fuse element has an alloy composition in which In is 15% or larger and smaller than 37%, Sn is 5% or larger and 28% or smaller, and balance Bi, and in which, with respect to each of reference points of 79°C ternary Bi-In-Sn eutectic point of 57.5%Bi-25.2%In-17.3%Sn and 81°C ternary Bi-In-Sn eutectic point of 54.0%Bi-29.7%In-16.3%Sn, a range of ±2%Bi, ±1%In, and ±1%Sn is excluded (namely, the range of 55.5% ≤ Bi ≤ 59.5%, 24.2% ≤ In ≤ 26.2%, and 16.3% ≤ Sn ≤ 18.3%, and that of 52% ≤ Bi ≤ 56%, 28.7% ≤ In ≤ 30.7%, and 15.3% ≤ Sn ≤ 17.3% are excluded) are as follows. In order to use a Bi-

In-Sn alloy because of the adaptability to the environment, and satisfy the requirement that the alloy type thermal fuse has an operating temperature of 75 to 120°C, the following points are satisfied with respect to the reference points of 79°C-eutectic and 81°C-eutectic: (i) the two eutectic points and the ranges adjacent to the eutectic points are excluded in order to eliminate solid phase transformation appearing in the eutectics; (ii) the amount of In is reduced in order to prevent In which is highly reactive, from reacting with a flux in the surface of the fuse element to be reduced, and reactive groups of the flux from forming an In salt; and (iii) although the composition shows a melt pattern having a wide solid-liquid coexisting region which is considerably separated from the eutectic points, the alloy composition exhibits a single maximum endothermic peak such as shown in (A) of Fig. 14 (according to the alloy composition, namely, the fuse element can operate in a concentrated temperature zone, and dispersion of the operating temperature can be set to be within an allowable range), and the maximum endothermic peak satisfies the requirement of an operating temperature of 75 to 120°C.

[0028]

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In the above, in interface zones respectively adjacent to the eutectic points in the remaining region excluding the range of  $\pm 2\% Bi$ ,  $\pm 1\% In$ , and  $\pm 1\% Sn$  with respect to each

of the 79°C ternary Bi-In-Sn eutectic point and the 81°C ternary Bi-In-Sn eutectic point, the melting point is close to the melting points of the eutectics (79 to 81°C), and also the DSC melt pattern is close to the melt patterns of the 79°C ternary Bi-In-Sn eutectic and 81°C ternary Bi-In-Sn eutectic. Therefore, requirement (iii) is satisfied. In addition, solid phase transformation in a range which is lower than the melting point can be eliminated, and hence requirement (i) is satisfied. Since the amount of In is small, also requirement (ii) is satisfied.

[0029]

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Each of the aboves will be further described.

(1) From a result of a DSC measurement of a 79°C ternary Bi-In-Sn eutectic alloy shown in Fig. 12 and that of a DSC measurement of an 81°C ternary Bi-In-Sn eutectic alloy shown 15 in Fig. 13, it is seen that the absorption amount of heat energy is sharply changed in the vicinity of the melting point because the solid phase is suddenly changed to the liquid phase, and, in the temperature zones of about 52 to 20 58°C and about 51 to 57°C which are lower than the melting point, the heat energy is absorbed and transformation occurs while maintaining the solid phase state. In the solid phase transformation, distortion is generated in accordance with a change of the phase state, and hence stress is pro-25 duced in the fuse element ends of which are fixed to lead conductors or electrodes. A thermal fuse is exposed to a heat cycle at a temperature which is lower than the operating temperature. As described above, a thermal fuse is requested to have predetermined heat cycle resistance, and to pass a heat cycle test in which one cycle is set to be between the normal temperature (the operating temperature - 20°C) and the room temperature or a below-freezing temperature (usually, -40°C). In the case of an operating temperature of 75 to 120°C, one cycle is set to be between (55 to 100°C) and -40°C, and the solid phase transformation zones (52 to 58°C) and (51 to 57°C) overlap with the cycle. Therefore, stress due to solid phase transformation is repetitively applied to the fuse element. When this state continues for a long period, a remarkable change of the resistance, breakage, or a malfunction is caused.

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In the invention, therefore, the range of ±2%Bi, ±1%In, and ±1%Sn with respect to each of the 79°C ternary Bi-In-Sn eutectic point and the 81°C ternary Bi-In-Sn eutectic point is excluded.

20 (2) In is more highly reactive than Bi and Sn, and reacts in the surface of a fuse element with reactive groups of the flux to produce an In salt. When the production rate is high, shift or impairment of the melting characteristic of the fuse element due to the reduced amount of In, and reduction of the activity of the flux remarkably occur to

impair the characteristics of the thermal fuse. In a thermal fuse, it is requested to evaluate the aging resistance, so that abnormality does not occur even when load, no-load, and humidified conditions are continued for a long term under an environment of a high temperature such as the holding temperature. Because of the impairment of the characteristics of the thermal fuse due to the reaction of In, however, it is very difficult to maintain the operation stability for a long period.

10 In the invention, therefore, the amount of In is set to be smaller than that in Patent Reference Documents 1 to 6 above or to be smaller than 37%. In this case, since the range of In smaller than 15% is excluded, the requirement of an operating temperature of 75 to 120°C is satisfied, and thinning to 300 μmφ can be performed with a high yield.

(3) In Bi-In-Sn alloys, there is an alloy having a melt pattern in which, even when deviated from a eutectic point or a eutectic line, or when the solid-liquid coexisting region is widened, the maximum endothermic peak is at one point in the wide solid-liquid coexisting region as shown in (A) of Fig. 14. In such an alloy, in the endothermic behavior in the melting process, the heat absorption amount difference at the maximum endothermic peak is very larger than that in another portion of the endothermic process, and all constituting elements have excellent wettability.

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Therefore, the wettability of the solid-liquid coexisting region at the maximum endothermic peak is sufficiently improved even before the completion of the liquidification, so that spheroid division of the thermal fuse element can be performed in the vicinity of the maximum endothermic peak.

In the invention, therefore, Sn is set to 5 to 28% so that, although deviated from the 79°C ternary Bi-In-Sn eutectic point and the 81°C ternary Bi-In-Sn eutectic point, the operating temperature is set to the range of 75 to 120°C with dispersion of an allowable range (±5°C).

[0030]

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In claim 1, one of the reference alloy compositions is that In is 25%, Sn is 20%, and a balance is Bi. The liquidus temperature is about 84°C, the solidus temperature is about 80°C, a result of a DSC measurement at a temperature rise rate of 5°C/min. is shown in Fig. 10, and the maximum endothermic peak is at about 82°C.

The other reference composition is that In is 30%, Sn 20 is 15%, and a balance is Bi. The liquidus temperature is about 86°C, the solidus temperature is about 81°C, a result of a DSC measurement at a temperature rise rate of 5°C/min. is shown in Fig. 11, and the maximum endothermic peak is at about 82°C.

In both the measurement results, an endothermic reac-

tion is not observed in a temperature region which is lower than the melting points observed in the DSC measurement result of the 79°C ternary Bi-In-Sn eutectic alloy shown in Fig. 12 and that of the 81°C ternary Bi-In-Sn eutectic alloy shown in Fig. 13, and there is no solid phase transformation which may cause a serious problem.

[0031]

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In the invention, 0.1 to 3.5 weight parts of one, or two or more elements selected from the group consisting of Ag, Au, Cu, Ni, Pd, Pt, Ga, Ge, and Sb are added to 100 weight parts of the alloy composition, in order to reduce the specific resistance of the alloy and improve the mechanical strength. When the addition amount is smaller than 0.1 weight parts, the effects cannot be sufficiently attained, and, when the addition amount is larger than 3.5 weight parts, the above-mentioned melting characteristic is hardly maintained.

With respect to a drawing process, further enhanced strength and ductility are provided so that drawing into a thin wire of 100 to 300 µm¢ can be easily conducted. In the case where the cohesive force of a fuse element alloy is considerably enhanced by the inclusion of In, even when a fuse element is insufficiently welded or bonded to lead conductors or the like, a superficial appearance in which the element is bonded is produced. The addition of the

element(s) can reduce the cohesive force, so that this defect can be eliminated, and the accuracy of the acceptance criterion in a test after welding can be improved.

It is known that a to-be-bonded material such as a metal material of the lead conductors, a thin-film material, or a particulate metal material in the film electrode migrates into the fuse element by solid phase diffusion. When the same element as the to-be-bonded material, such as Ag, Au, Cu, or Ni is previously added to the fuse element, 10 the migration can be suppressed. Therefore, an influence of the to-be-bonded material which may originally affect the characteristics (for example, Ag, Au, or the like causes local reduction or dispersion of the operating temperature due to the lowered melting point, and Cu, Ni, or 15 the like causes dispersion of the operating temperature or an operation failure due to an increased intermetallic compound layer formed in the interface between different phases) is eliminated, and the thermal fuse can be assured to normally operate, without impairing the function of the 2.0 fuse element.

[0032]

The fuse element of the alloy type thermal fuse of the invention can be usually produced by a method in which a billet is produced, the billet is shaped into a stock wire by an extruder, and the stock wire is drawn by a dice to a

wire. The outer diameter is 100 to 800  $\mu m \phi$ , preferably, 300 to 600  $\mu m \phi$ . The wire can be finally passed through calender rolls so as to be used as a flat wire.

Alternatively, the fuse element may be produced by the rotary drum spinning method in which a cylinder containing cooling liquid is rotated, the cooling liquid is held in a layer-like manner by a rotational centrifugal force, and a molten material jet ejected from a nozzle is introduced into the cooling liquid layer to be cooled and solidified, thereby obtaining a thin wire member.

In the production, the alloy composition is allowed to contain inevitable impurities which are produced in productions of metals of raw materials and also in melting and stirring of the raw materials.

15 [0033]

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The invention may be implemented in the form of a thermal fuse serving as an independent thermoprotector. Alternatively, the invention may be implemented in the form in which a thermal fuse element is connected in series to a semiconductor device, a capacitor, or a resistor, a flux is applied to the element, the flux-applied fuse element is placed in the vicinity of the semiconductor device, the capacitor, or the resistor, and the fuse element is sealed together with the semiconductor device, the capacitor, or the resistor by means of resin mold, a case, or the like.

[0034]

The thermal fuse of the invention is useful particularly as a thermoprotector for a secondary battery of a high energy density such as a lithium battery or a lithium polymer battery, and configured preferably as a thin thermal fuse of the tape type in view of the accommodation space in a battery pack.

Fig. 1 is a view showing an embodiment of a thin thermal fuse.

Referring to Fig. 1, 1 denotes flat lead conductors, 10 and 2 denotes a fuse element of claim 1 or 2 which is bonded between upper faces of tip ends of the flat lead conductors 1 by welding or the like. In the welding process, spot resistance welding, laser welding, or the like 15 can be used. The reference numeral 41 denotes a lower resin film, and 42 denotes an upper resin film. Front end portions of the flat lead conductors 1, and the fuse element 2 are sandwiched between the resin films 41, 42, and the peripheral portion of the upper resin film 42 is seal-20 ingly bonded to the lower resin film 41 which is horizontally held. The reference numeral 3 denotes a flux applied to the periphery of the fuse element 2.

The thin thermal fuse is produced in the following manner. The fuse element is bonded between the upper faces of the tip ends of the flat lead conductors by spot resis-

tance welding, laser welding, or the like. Front end portions of the flat lead conductors 1, and the fuse element 2 are sandwiched between the lower and upper resin films 41, 42, the lower resin film 31 is horizontally held on a platform, and end portions of the upper resin film 42 are 5 pressed by a releasable chip such as a ceramic chip to cause end portions 421 of the upper resin film 42 to be in press contact with the flat lead conductors 1. Under this state, the flat lead conductors 1 are heated so that the contact faces of the flat lead conductors 1 and end por-10 tions (portions pressed by the releasable chip) of the resin films 41, 42 are fusingly bonded together. ter, faces of the resin films 41, 42 which are directly in contact with each other are sealingly bonded together. timing of applying the flux 3 is set to that before the 15 fuse element 2 is sandwiched between the lower and upper resin films 41, 42, or that after the contact faces of the flat lead conductors 1 and end portions of the resin films 41, 42 are fusingly bonded together and before faces of the resin films 41, 42 which are directly in contact with each 20 other are sealingly bonded together.

[0035]

The flat lead conductors can be heated by electromagnetic induction heating, contact between a heat plate and 25 the lead conductors, or the like. In electromagnetic induction heating, particularly, high-frequency magnetic fluxes cross tip end portions of the lead conductors welded to end portions of the fuse element, through the lower or upper resin film to concentrically heat the tip end portions. Therefore, electromagnetic induction heating is advantageous from the viewpoint of the heat efficiency. The seal bonding between the faces of the lower and upper resin films 41, 42 which are directly in contact with each other can be performed by ultrasonic fusion, high-frequency induction heating fusion, heat plate contact fusion, or the like.

[0036]

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Fig. 2 is a view showing another embodiment of a thin thermal fuse.

Referring to Fig. 2, 41 denotes a resin base film, and
1 denotes flat lead conductors in each of which a front end
portion is fixed to the rear face of the base film 41 and a
part 10 of the front portion is exposed from the upper face
of the base film 41. The reference numeral 2 denotes a

20 fuse element of claim 1 or 2 which is bonded between the
exposed portions 10 of the flat lead conductors 1 by welding or the like. In the welding process, spot resistance
welding, laser welding, or the like can be used. The reference numeral 42 denotes a resin cover film which is sealingly bonded in a peripheral portion to the base film 41

that is horizontally held. The reference numeral 3 denotes a flux applied to the periphery of the fuse element 2.

[0037]

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The exposure of the portions 10 of the flat lead conductors to the surface of the base film 41 may be conducted by, for example, one of the following methods. A projection is previously formed in the front end portion of each of the flat lead conductors by a squeezing process, the front end portions of the flat lead conductors are fusingly bonded under heating to the rear face of the base film, and the projections are protrudingly bonded to the base film. Alternatively, the front end portions of the flat lead conductors are fusingly bonded under heating to the rear face of the base film, and parts of the front end portions of the flat lead conductors are caused to appear from the surface of the base film by a squeezing process.

The thin thermal fuse is produced in the following manner. On a platform, the fuse element 2 is bonded between the lead conductor exposed portions 10 of the surface of the resin base film 41 by spot resistance welding, laser welding, or the like. The flux 3 is then applied to the fuse element 2. Thereafter, the resin cover film 42 is placed, and the peripheral portion of the film is sealingly bonded to the periphery of the resin base film 41.

The seal bonding of the peripheral portion of the

resin cover film 42 to the resin base film 41 can be performed by ultrasonic fusion, high-frequency induction heating fusion, heat plate contact fusion, or the like.

[0038]

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The thermal fuse of the invention may be realized in the form of a fuse of the case type, the substrate type, or the like.

Fig. 3 shows an alloy type thermal fuse of the cylindrical case type according to the invention. A fuse element 2 of claim 1 or 2 is connected between a pair of lead conductors 1 by, for example, welding. A flux 3 is applied to the fuse element 2. The flux-applied fuse element is passed through an insulating tube 4 which is excellent in heat resistance and thermal conductivity, for example, a ceramic tube. Gaps between the ends of the insulating tube 4 and the lead conductors 1 are sealingly closed by a sealing agent 5 such as a cold-setting epoxy resin.

[0039]

element 2 of claim 1 or 2 is connected between tip ends of parallel lead conductors 1 by, for example, welding. A flux 3 is applied to the fuse element 2. The flux-applied fuse element is enclosed by an insulating case 4 in which one end is opened, for example, a ceramic case. The opening of the insulating case 4 is sealingly closed by sealing

agent 5 such as a cold-setting epoxy resin.

[0040]

Fig. 5 shows a fuse of the radial resin dipping type. A fuse element 2 of claim 1 or 2 is bonded between tip ends of parallel lead conductors 1 by, for example, welding. A flux 3 is applied to the fuse element 2. The flux-applied fuse element is dipped into a resin solution to seal the element by an insulative sealing agent such as an epoxy resin 5.

10 [0041]

Fig. 6 shows a fuse of the substrate type. A pair of film electrodes 1 are formed on an insulating substrate 4 such as a ceramic substrate by printing conductive paste. Lead conductors 11 are connected respectively to the elec-15 trodes 1 by, for example, welding or soldering. element 2 of claim 1 or 2 is bonded between the electrodes 1 by, for example, welding. A flux 3 is applied to the fuse element 2. The flux-applied fuse element is covered with a sealing agent 5 such as an epoxy resin. The conduc-20 tive paste contains metal particles and a binder. ample, Ag, Ag-Pd, Ag-Pt, Au, Ni, or Cu may be used as the metal particles, and a material containing a glass frit, a thermosetting resin, and the like may be used as the binder.

The invention may be implemented in the form in which a heating element for fusing off the fuse element is additionally disposed on the alloy type thermal fuse. As shown in Fig. 7, for example, a conductor pattern 100 having fuse element electrodes 1 and resistor electrodes 10 is formed on an insulating substrate 4 such as a ceramic substrate by printing conductive paste, and a film resistor 6 is disposed between the resistor electrodes 10 by applying and baking resistance paste (e.g., paste of metal oxide powder such as ruthenium oxide). Lead conductors 11 are bonded respectively to the electrodes 1 and 10. A fuse element 2 of claim 1 or 2 is bonded between the fuse element electrodes 1 by, for example, welding. A flux 3 is applied to The flux-applied fuse element 2 and the fuse element 2. the film resistor 6 are covered with a sealing agent 5 such as an epoxy resin.

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In the thermal fuse having an electric heating element, a precursor causing abnormal heat generation of an appliance is detected, the film resistor is energized to generate heat in response to a signal indicative of the detection, and the fuse element is fused off by the heat generation.

The heating element may be disposed on the upper face of an insulating substrate. A heat-resistant and thermal-conductive insulating film such as a glass baked film is

formed on the heating element. A pair of electrodes are disposed, flat lead conductors are connected respectively to the electrodes, and the fuse element is connected between the electrodes. A flux covers a range over the fuse element and the tip ends of the lead conductors. An insulating cover is placed on the insulating substrate, and the periphery of the insulating cover is sealingly bonded to the insulating substrate by an adhesive agent.

[0043]

Among the alloy type thermal fuses, those of the type in which the fuse element is directly bonded to the lead conductors (Figs. 1 to 5) may be configured in the following manner. At least portions of the lead conductors where the fuse element is bonded are covered with a thin film of Sn or Ag (having a thickness of, for example, 15 μm or smaller, preferably, 5 to 10 μm) (by plating or the like), thereby enhancing the bonding strength with respect to the fuse element.

In the alloy type thermal fuses, there is a possibility that a metal material or a thin film material in the
lead conductors, or a particulate metal material in the
film electrode migrates into the fuse element by solid
phase diffusion. As described above, however, the characteristics of the fuse element can be sufficiently maintained by previously adding the same element as the thin

film material into the fuse element.

[0044]

As the flux, a flux having a melting point which is lower than that of the fuse element is generally used. For example, useful is a flux containing 90 to 60 weight parts of rosin, 10 to 40 weight parts of stearic acid, and 0 to 3 weight parts of an activating agent. In this case, as the rosin, a natural rosin, a modified rosin (for example, a hydrogenated rosin, an inhomogeneous rosin, or a polymerized rosin), or a purified rosin thereof can be used. As the activating agent, hydrochloride or hydrobromide of an amine such as diethylamine, or an organic acid such as adipic acid can be used.

[0045]

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As the resin film of the thin thermal fuse, useful is a plastic film having a thickness of about 100 to 500 μm, for example, a film of: an engineering plastic such as polyethylene terephtalate, polyethylene naphthalate, polyamide, polyimide, polybuthylene terephtalate, polyphenylene oxide, polyethylene sulfide, or polysulfone; an engineering plastic such as polyacetal, polycaronate, polyphenylene sulfide, polyoxybenzoyl, polyether ether ketone, or polyether imide; polypropylene; polyvinyl chloride; polyvinyl acetate; polymetyl methacrylate; polyvinylidene chloride; polytetrafluoroethylene; ethylene polytetrafluoroethylene

copolymer; ethylene-vinyl acetate copolymer (EVA); AS resin; ABS resin; ionomer; AAS resin; or ACS resin.

[0046]

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Among the above-described alloy type thermal fuses, in the fuse of the cylindrical case type, the arrangement in which the lead conductors 1 are placed so as not to be eccentric to the cylindrical case 4 as shown in (A) of Fig. 8 is a precondition to enable the normal spheroid division shown in (B) of Fig. 8. When the lead conductors are eccentric as shown in (C) of Fig. 8, the flux (including a charred flux) and scattered alloy portions easily adhere to the inner wall of the cylindrical case after an operation as shown in (D) of Fig. 8. As a result, the insulation resistance is lowered, and the dielectric breakdown characteristic is impaired.

In order to prevent such disadvantages from being produced, as shown in (A) of Fig. 9, a configuration is effective in which ends of the lead conductors 1 are formed into a disk-like shape d, and ends of the fuse element 2 are bonded to the front faces of the disks d, respectively (by, for example, welding). The outer peripheries of the disks are supported by the inner face of the cylindrical case, and the fuse element 2 is positioned so as to be substantially concentrical with the cylindrical case 4 [in (A) of Fig. 9, 3 denotes a flux applied to the fuse element 2, 4

denotes the cylindrical case, 5 denotes a sealing agent such as an epoxy resin, and the outer diameter of each disk is approximately equal to the inner diameter of the cylindrical case]. In this instance, as shown in (B) of Fig. 9, molten portions of the fuse element spherically aggregate on the front faces of the disks d, thereby preventing the flux (including a charred flux) from adhering to the inner face of the case 4.

[0047]

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10 [Examples]

In the following examples and comparative examples, alloy type thermal fuses of the thin type shown in Fig. 1 were used. A polybuthylene terephtalate film having a thickness of 200  $\mu m$ , a width of 5 mm, and a length of 10 mm was used as the lower resin film 31 and the upper resin film 32. A copper conductor having a thickness of 150  $\mu m$ , a width of 3 mm, and a length of 20 mm was used as the flat lead conductors 1. The fuse element 2 has a length of 4 mm and an outer diameter of 300  $\mu m \varphi$ . A compound of 80 weight parts of natural rosin, 20 weight parts of stearic acid, and 1 weight part of hydrobromide of diethylamine was used as the flux.

The solidus and liquidus temperatures of a fuse element were measured by a DSC at a temperature rise rate of  $5^{\circ}\text{C/min}$ .

[0048]

Fifty specimens were used. Each of the specimens was immersed into an oil bath in which the temperature was raised at a rate of  $1^{\circ}$ C/min., while supplying a current of 0.1 A to the specimen, and the temperature T0 of the oil when the current supply was interrupted by blowing-out of the fuse element was measured. A temperature of T0 -  $2^{\circ}$ C was determined as the element temperature at an operation of the thermal fuse.

10 [0049]

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The heat cycle resistance was evaluated in the following manner. Fifty specimens were used. A heat cycle test in which each cycle is configured by (operating temperature - 20°C) × 30 min. and -40°C × 30 min. was conducted 1,000 cycles. The resistance was measured. When an abnormality such as that the resistance is changed remarkably or by 50% or more, that the fuse element is broken, or that, in an after-test operation test, the operating temperature is deviated by ±7°C or more from the initial operating temperature or the thermal fuse does not operate was observed even in one specimen, the heat cycle resistance was evaluated as unacceptable. When an abnormality was not observed in all the specimens, the heat cycle resistance was evaluated as acceptable.

The aging resistance was evaluated by a load aging

test. Fifty specimens were used. The specimens were exposed to a high-temperature environment of (operating temperature - 20°C) for 20,000 hours while supplying a rated current. Thereafter, the resistance was measured. When an abnormality such as that the resistance is changed remarkably or by 50% or more, that the fuse element is broken, or that, in an after-test operation test, the operating temperature is deviated by ±7°C or more from the initial operating temperature or the thermal fuse does not operate was observed even in one specimen, the aging resistance was evaluated as unacceptable. When an abnormality was not observed in all the specimens, the aging resistance was evaluated as acceptable.

With respect to the drawability of a fuse element, a process of drawing to 300 µm¢ under the conditions of an area reduction per dice of 6.5%, and a drawing speed of 50 m/min. was conducted. When the drawing process was conducted with satisfactory yield without causing a constricted portion or a breakage, the drawability was evaluated as O. When a constricted portion or a breakage was caused so that the sectional area was not stabilized nor the continuity of the drawing was not ensured, the drawability was evaluated as ×.

[0050]

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A fuse element having an alloy composition of 25% In, 20% Sn, and balance Bi was produced. The wire drawability to a fuse element was  $\mathbf{O}$ .

Fig. 10 shows a result of a DSC measurement of the fuse element. The liquidus temperature was about 84°C, the solidus temperature was about 80°C, and the maximum endothermic peak temperature was about 81°C. Since the alloy composition is close to the 79°C ternary Bi-In-Sn eutectic point of 57.5%Bi-25.2%In-17.3%Sn, the DSC measurement result belongs to the pattern of (B) Fig. 14. However, the solid phase transformation zone does not exist in the temperature side which is lower than the solidus temperature.

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The fuse element temperature at an operation of a thermal fuse was  $82 \pm 1^{\circ}\text{C}$ . Therefore, it is apparent that the fuse element temperature at an operation of a thermal fuse approximately coincides with the maximum endothermic peak temperature of about  $82^{\circ}\text{C}$ .

The example passed both the load aging test and the heat cycle test. The reason of the pass in the load aging test is estimated as follows. Since the amount of In is as small as 25%, the reaction of In with the flux was suppressed, and the variation of the alloy composition and the reduction of the activity of the flux were conducted at a very small degree. As apparent from the DSC measurement

result, solid phase transformation was not observed in the temperature side which is lower than the solidus temperature. Therefore, the pass in the heat cycle test coincides with the estimation.

5 [0051]

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[Example 2]

A fuse element having an alloy composition of 30% In, 15% Sn, and balance Bi was produced.

The wire drawability to a fuse element was O.

10 Fig. 11 shows a result of a DSC measurement of the fuse element. The liquidus temperature was about 86°C, the solidus temperature was about 81°C, and the maximum endothermic peak temperature was about 82°C. Since the alloy composition is close to the 79°C ternary Bi-In-Sn eutectic point of 54.0%Bi-29.7%In-16.3%Sn, the DSC measurement result belongs to the pattern of (B) Fig. 14. However, the solid phase transformation zone does not exist in the temperature side which is lower than the solidus temperature.

The fuse element temperature at an operation of a thermal fuse was  $82 \pm 1^{\circ}\text{C}$ . Therefore, it is apparent that the fuse element temperature at an operation of a thermal fuse approximately coincides with the maximum endothermic peak temperature of about  $82^{\circ}\text{C}$ .

The example passed both the load aging test and the 25 heat cycle test. The reason of the pass in the load aging

test is estimated as follows. Since the amount of In is as small as 30%, the reaction of In with the flux was suppressed, and the variation of the alloy composition and the reduction of the activity of the flux were conducted at a very small degree in the same manner as Example 1. As apparent from the DSC measurement result, in the same manner as Example 1, solid phase transformation was not observed in the temperature side which is lower than the solidus temperature. Therefore, the pass in the heat cycle test coincides with the estimation.

[0052]

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[Examples 3 to 7]

The examples were conducted in the same manner as Example 1 except that the alloy composition in Example 1 was changed as listed in Table 1.

In all the examples, good wire drawability was obtained.

The solidus and liquidus temperatures of the examples are shown in Table 1. The fuse element temperatures at an operation are as shown in Table 1, have dispersion of  $\pm 3^{\circ}\text{C}$  or smaller, and are in the solid-liquid coexisting region.

The melt pattern of the fuse element of each example belongs to the pattern of (A) of Fig. 14, and the solid-liquid coexisting region is wide. However, the single endothermic peak exists and is sharp. As a result, disper-

sion of the operating temperature can be set to be  $\pm 3\,^{\circ}\text{C}$  or smaller.

The examples passed the load aging test. The reason of the pass in the load aging test is estimated as follows.

5 Since the amount of In is as small as 15 to 35%, the reaction of In with the flux was suppressed, and the variation of the alloy composition and the reduction of the activity of the flux were conducted at a very small degree in the same manner as Example 1.

The examples passed also the heat cycle test. From results of DSC measurements, it was confirmed that solid phase transformation does not exist in the temperature side which is lower than the solidus temperature. This coincides with the estimation.

15 [Table 1]

Table 1

	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
In (%)	15	20	25	30	35
Sn (%)	5	5	5	5	5
Bi	Balance	Balance	Balance	Balance	Balance
Solidus tempera-					
ture	79	79	79	80	84
(°C)					
Liquidus tempera-					!
ture (°C)	194	171	144	109	105
Wire drawability	0	0	0	0	0
Element tempera-					
ture	85 ± 1	84 ± 1	92 ± 2	95 ± 3	98 ± 3
at operation (°C)					
Heat cycle resis-	Daniel	,	,		
tance test	Passed	Passed	Passed	Passed	Passed
Load aging test	Passed	Passed	Passed	Passed	Passed

[0053]

[Examples 8 to 11]

The examples were conducted in the same manner as Example 1 except that the alloy composition in Example 1 was changed as listed in Table 2.

In all the examples, good wire drawability was obtained.

The solidus and liquidus temperatures of the examples are shown in Table 2. The fuse element temperatures at an operation are as shown in Table 2, have dispersion of  $\pm 1^{\circ}$ C or smaller, and are in the solid-liquid coexisting region.

The melt pattern of the fuse element of each example belongs to the pattern of (A) of Fig. 14, and the solid-liquid coexisting region is wide. However, the single endothermic peak exists and is sharp. As a result, dispersion of the operating temperature can be set to be  $\pm 1^{\circ}$ C or smaller.

The examples passed the load aging test. The reason of the pass in the load aging test is estimated as follows. Since the amount of In is as small as 15 to 35%, the reaction of In with the flux was suppressed, and the variation of the alloy composition and the reduction of the activity of the flux were conducted at a very small degree in the same manner as Example 1.

The examples passed also the heat cycle test. From results of DSC measurements, it was confirmed that solid phase transformation does not exist in the temperature side which is lower than the solidus temperature. This coincides with the estimation.

[Table 2]

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Table 2

	Ex. 8	Ex. 9	Ex. 10	Ex. 11
In (%)	15	20	25	35
Sn (%)	15	15	15	15
Bi	Balance	Balance	Balance	Balance
Solidus temperature	7.0	0.0		60
(°C)	79	80	80	69
Liquidus tempera-	158	134	105	84
ture (°C)	130	134	105	84
Wire drawability	0	0	0	0
Element temperature		0.6 1 1		70 1 1
at operation (°C)	86 ± 1	86 ± 1	83 ± 1	79 ± 1
Heat cycle resistance test	Passed	Passed	Passed	Passed
Load aging test	Passed	Passed	Passed	Passed

[0054]

## 5 [Examples 12 to 16]

The examples were conducted in the same manner as Ex-ample 1 except that the alloy composition in Example 1 was changed as listed in Table 2.

In all the examples, good wire drawability was ob10 tained.

The solidus and liquidus temperatures of the examples are shown in Table 3. The fuse element temperatures at an

operation are as shown in Table 3, have dispersion of  $\pm 3^{\circ}$ C or smaller, and are in the solid-liquid coexisting region.

The melt pattern of the fuse element of each example belongs to the pattern of (A) of Fig. 14, and the solid-liquid coexisting region is wide. However, the single endothermic peak exists and is sharp. As a result, dispersion of the operating temperature can be set to be  $\pm 3^{\circ}\text{C}$  or smaller.

The examples passed the load aging test. The reason of the pass in the load aging test is estimated as follows. Since the amount of In is as small as 15 to 35%, the reaction of In with the flux was suppressed, and the variation of the alloy composition and the reduction of the activity of the flux were conducted at a very small degree in the same manner as Example 1.

The examples passed also the heat cycle test. From results of DSC measurements, it was confirmed that solid phase transformation does not exist in the temperature side which is lower than the solidus temperature. This coincides with the estimation.

[Table 3]

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Table 3

	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16
In (%)	15	20	25	30	35
Sn (%)	25	25	25	25	25
Bi	Balance	Balance	Balance	Balance	Balance
Solidus tempera-					
ture	79	79	79	78	77
(°C)					
Liquidus tempera-	126	107	107	107	104
ture (°C)					
Wire drawability	0	0	0	0	0
Element tempera-					
ture	94 ± 3	83 ± 1	82 ± 1	81 ± 1	80 ± 3
at operation (°C)					
Heat cycle resis-	D = = = 1				
tance test	Passed	Passed	Passed	Passed	Passed
Load aging test	Passed	Passed	Passed	Passed	Passed

[0055]

## 5 [Example 17]

The example was conducted in the same manner as Example 1 except that an alloy composition in which 1 weight part of Ag was added to 100 weight parts of the alloy composition of Example 1 was used as that of a fuse element.

A wire member for a fuse element of 300 µmφ was produced under conditions in which the area reduction per dice was 8% and the drawing speed was 80 m/min., and which are severer than those of the drawing process of a wire member for a fuse element in Example 1. However, no wire breakage occurred, and problems such as a constricted portion were not caused, with the result that the example exhibited excellent workability.

The solidus temperature was 79°C, and the maximum endothermic peak temperature and the fuse element temperature
at an operation of a thermal fuse were lowered only by
about 1°C as compared with those in Example 1. Namely, it
was confirmed that the operating temperature and the melting characteristic can be held without being largely differentiated from those of Example 1.

The example passed both the heat cycle test and the load aging test. It is estimated that the consideration results were maintained because the addition amount of Ag is as small as 1 weight part.

It was confirmed that the above-mentioned effects are obtained in the range of the addition amount of 0.1 to 3.5 weight parts of Ag.

In the case where the metal material of the lead conductors to be bonded, a thin film material, or a particulate metal material in the film electrode is Ag, it was

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confirmed that, when the same element or Ag is previously added as in the example, the metal material can be prevented from, after a fuse element is bonded, migrating into the fuse element with time by solid phase diffusion, and local reduction or dispersion of the operating temperature due to solid phase diffusion can be eliminated.

[0056]

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[Examples 18 to 25]

The examples were conducted in the same manner as Ex
ample 1 except that an alloy composition in which 0.5

weight parts of respective one of Au, Cu, Ni, Pd, Pt, Ga,

Ge, and Sb were added to 100 weight parts of the alloy com
position of Example 1 was used as that of a fuse element.

It was confirmed that, in the same manner as the metal addition of Ag in Example 17, also the addition of Au, Cu, Ni, Pd, Pt, Ga, Ge, or Sb realizes excellent wire drawability, the operating temperature and melting characteristic are not largely different from those of Example 1, the examples passed the heat cycle test and the load aging test, and solid phase diffusion between metal materials of the same kind can be suppressed.

It was confirmed that the above-mentioned effects are obtained in the range of the addition amount of 0.1 to 3.5 weight parts of respective one of Au, Cu, Ni, Pd, Pt, Ga, Ge, and Sb.

[0057]

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[Comparative Example 1]

The comparative example was conducted in the same manner as Example 1 except that the composition of the fuse element in Example 1 was changed to 25.2% In, 17.3% Sn, and the balance Bi.

The wire drawability was satisfactory. The fuse element temperature at an operation of a thermal fuse was  $81 \pm 1^{\circ}\text{C}$ . Fig. 12 shows a result of a DSC measurement. It was expected to produce excellent thermal fuses in which the solid-liquid coexisting region is narrow and the operating temperature is less dispersed. However, solid phase transformation was observed between temperatures of 52 to  $58^{\circ}\text{C}$ .

The resistances of specimens which were subjected to 1,000 cycles of a heat cycle test (in which each cycle is configured by  $60^{\circ}\text{C} \times 30$  min. and  $-40^{\circ}\text{C} \times 30$  min.) were measured. As a result, a resistance change of 50% or more, and a breakage often occurred, and the result of the heat cycle test was  $\times$ . This was caused by the following reason. The solid phase transformation zone overlaps with the temperature zone of the heat cycles, and stress due to solid phase transformation was repetitively produced.

[0058]

[Comparative Example 2]

25 The comparative example was conducted in the same man-

ner as Example 1 except that the composition of the fuse element in Example 1 was changed to 29.7% In, 16.3% Sn, and the balance Bi.

The wire drawability was satisfactory. The fuse element temperature at an operation of a thermal fuse was 81 ± 1°C. Fig. 13 shows a result of a DSC measurement. It was expected to produce excellent thermal fuses in which the solid-liquid coexisting region is narrow and the operating temperature is less dispersed. However, solid phase transformation was observed between temperatures of 51 to 57°C.

The resistances of specimens which were subjected to 1,000 cycles of a heat cycle test (in which each cycle is configured by 60°C × 30 min. and -40°C × 30 min.) were measured. As a result, in the same manner as Comparative Example 1, a resistance change of 50% or more, and a breakage often occurred, and the result of the heat cycle test was x. This was caused by the following reason. In the same manner as Comparative Example 1, the solid phase transformation zone overlaps with the temperature zone of the heat cycles, and stress due to solid phase transformation was repetitively produced.

[0059]

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[Comparative Example 3]

The comparative example was conducted in the same man25 ner as Example 1 except that the composition of the fuse

element in Example 1 was changed to 40% In, 20% Sn, and the balance Bi.

The wire drawability was satisfactory. As a result of a DSC measurement, the solid-liquid coexisting region is narrow. As a result of the measurement of an operating temperature, dispersion of the operating temperature was within the allowable range. The result of a heat cycle test was acceptable.

The resistances of specimens which had been subjected to a load aging test for 7,000 hours were measured. A remarkable increase of the resistance which is 50% or more was observed. The operating temperature was measured. a result, in many specimens, the operating temperature was largely deviated from the range of the initial operating temperature ±7°C. The reasons of the above are estimated as In was consumed by the flux, and the specific resistance of the fuse element was increased. Since the amount of In in the alloy was reduced, the operating temperature was varied. Since the reactive groups were used for producing an In salt, the activity of the flux was reduced, so that spheroid division of the molten alloy was not satisfactorily conducted.

[0060]

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[Comparative Example 4]

The comparative example was conducted in the same man-

ner as Example 1 except that the composition of the fuse element in Example 1 was changed to 10% In, 20% Sn, and the balance Bi.

A process of drawing to 300  $\mu m \varphi$  was attempted. However, breakage frequently occurred, and the wire drawability was  $\times$ .

A thin wire of 300  $\mu m \varphi$  was obtained by the rotary drum spinning method to be formed as a fuse element.

The DSC measurement result of the fuse element belongs to the melt pattern of (C) of Fig. 14. The fuse element temperature at an operation was measured. As a result, dispersion was larger than the allowable range of  $\pm 5^{\circ}$ C, and the fuse element was not able to be used as a thermal fuse.

The reasons of the large dispersion of the operating temperature are estimated as follows. The heat energy is slowly absorbed. The wettability is not suddenly changed. The point of a division operation of the fuse element is not determined in a narrow range.

[0061]

20 [Comparative Example 5]

The comparative example was conducted in the same manner as Example 1 except that the composition of the fuse element in Example 1 was changed to 20% In, 35% Sn, and the balance Bi.

A drawing process was smoothly conducted, and the wire

drawability was O.

In the result of a DSC measurement, the solid-liquid coexisting region is wide, the heat energy is slowly absorbed in the solid-liquid coexisting region, and the wettability is not suddenly changed. The DSC measurement result belongs to the melt pattern of (C) of Fig. 14.

The fuse element temperature at an operation was measured. As a result, dispersion was larger than the allowable range of  $\pm 5^{\circ}\text{C}$ , and the fuse element was not able to be used as a thermal fuse.

The reason of the large dispersion of the operating temperature is identical with that of Comparative Example 4.

[0062]

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[Comparative Example 6]

The comparative example was conducted in the same manner as Example 1 except that the composition of the fuse element in Example 1 was changed to 52% In and the balance Bi.

20 The wire drawability was satisfactory. As a result of a DSC measurement, the solid-liquid coexisting region is narrow. As a result of the measurement of an operating temperature, dispersion of the operating temperature was very small. The result of a heat cycle test was acceptable.

The resistances of specimens which had been subjected to a load aging test for 7,000 hours were measured. A remarkable increase of the resistance which is 50% or more was observed. The operating temperature was measured. a result, in many specimens, the operating temperature was largely deviated from the range of the initial operating temperature  $\pm 7^{\circ}$ C. The reasons of the above are estimated as In was consumed by the flux, and the specific refollows. sistance of the fuse element was increased. Since the amount of In in the alloy was reduced, the operating temperature was varied. Since the reactive groups were used for producing an In salt, the activity of the flux was reduced, so that spheroid division of the molten alloy was not satisfactorily conducted.

15 [0063]

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[Comparative Example 7]

The comparative example was conducted in the same manner as Example 1 except that the composition of the fuse element in Example 1 was changed to 52% In and the balance Sn.

The wire drawability was satisfactory. As a result of a DSC measurement, the solid-liquid coexisting region is narrow. As a result of the measurement of an operating temperature, dispersion of the operating temperature was very small. The result of a heat cycle test was accept-

able.

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The resistances of specimens which had been subjected to a load aging test for 7,000 hours were measured. A remarkable increase of the resistance which is 50% or more was observed. The operating temperature was measured. As a result, in many specimens, the operating temperature was largely deviated from the range of the initial operating temperature ±7°C. The reasons of the above are estimated as follows. In was consumed by the flux, and the specific resistance of the fuse element was increased. Since the amount of In in the alloy was reduced, the operating temperature was varied. Since the reactive groups were used for producing an In salt, the activity of the flux was reduced, so that spheroid division of the molten alloy was not satisfactorily conducted.

[0064]

[Effects of the Invention]

According to the material for a thermal fuse element and the thermal fuse of the invention, a small and thin alloy type thermal fuse can be provided in which a Bi-In-Sn alloy that does not contain a metal harmful to a living body is used as a fuse element, the operating temperature is 75 to 120°C, the initial operating characteristic is maintained, and excellent heat cycle and aging resistances are attained for a long term.

[0065]

According to the material for a thermal fuse element and the alloy type thermal fuse of claim 2 of the invention, since a fuse element can be further thinned because of the excellent wire drawability of the material for a thermal fuse element, the thermal fuse can be advantageously miniaturized and thinned. Even in the case where an alloy type thermal fuse is configured by bonding a fuse element to a to-be-bonded material which may originally exert an influence, a normal operation can be assured while maintaining the performance of the fuse element. Therefore, the thermal fuse is particularly useful as a thin thermoprotector for protecting a secondary battery which is requested to be thinned because of attachment to a battery pack.

[0066]

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According to the alloy type thermal fuses of claims 3 to 10 of the invention, particularly, the above effects can be assured in a thin thermal fuse of the tape type, a thermal fuse of the cylindrical case type, a thermal fuse of the substrate type, a thermal fuse having an electric heating element, a thermal fuse or a thermal fuse having an electric heating element in which lead conductors are plated by Sn, Ag, or the like, and a thermal fuse of the cylindrical case type in which ends of the lead conductors

have a disk-like shape, whereby the usefulness of such a thermal fuse can be further enhanced.

[Brief Description of the Drawings]

5 [Fig. 1]

Fig. 1 is a view showing an example of the alloy type thermal fuse of the invention.

[Fig. 2]

Fig. 2 is a view showing another example of the alloy 10 type thermal fuse of the invention.

[Fig. 3]

Fig. 3 is a view showing a further example of the alloy type thermal fuse of the invention.

[Fig. 4]

15 Fig. 4 is a view showing a still further example of the alloy type thermal fuse of the invention.

[Fig. 5]

Fig. 5 is a view showing a still further example of the alloy type thermal fuse of the invention.

20 [Fig. 6]

Fig. 6 is a view showing a still further example of the alloy type thermal fuse of the invention.

[Fig. 7]

Fig. 7 is a view showing a still further example of the alloy type thermal fuse of the invention.

[Fig. 8]

Fig. 8 is a view showing an alloy type thermal fuse of the cylindrical case type and its operation state.

[Fig. 9]

Fig. 9 is a view showing a still further example of the alloy type thermal fuse of the invention.

[Fig. 10]

Fig. 10 is a view showing a result of a DSC measurement of a fuse element of Example 1.

10 [Fig. 11]

Fig. 11 is a view showing a result of a DSC measurement of a fuse element of Example 2.

[Fig. 12]

Fig. 12 is a view showing a result of a DSC measure-15 ment of a 79°C ternary Bi-In-Sn eutectic alloy.

[Fig. 13]

Fig. 13 is a view showing a result of a DSC measurement of an 81°C ternary Bi-In-Sn eutectic alloy.

[Fig. 14]

Fig. 14 is a view showing various melt patterns of a ternary Sn-In-Bi alloy.

[Description of Reference Numerals]

- lead conductors or film electrodes
- 25 2 fuse element

- 3 flux
- 4 insulating tube
- 41 resin film
- 42 resin film
- 5 5 sealing agent
  - 6 film resistor

[Document Name]

ABSTRACT

[Summary]

[Object]

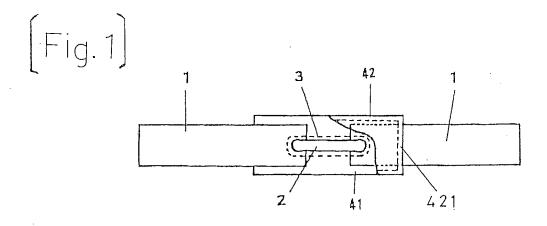
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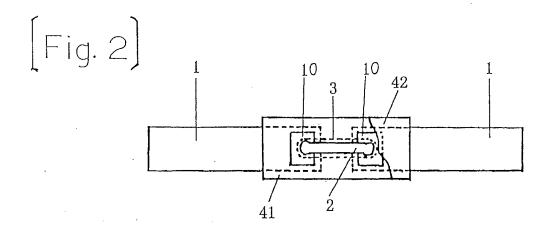
The invention provides an alloy type thermal fuse of an operating temperature of 75 to 120°C in which a fuse element of a Bi-In-Sn alloy is used, excellent aging and heat cycle resistances for a long term can be ensured, and satisfactory operating characteristic can be ensured.

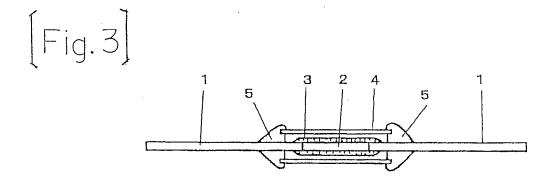
[Solution to the Problems]

A material for a thermal fuse element has an alloy composition in which In is 15% or larger and smaller than 37%, Sn is 5% or larger and 28% or smaller, and balance Bi, and in which, with respect to each of reference points of ternary Bi-In-Sn eutectic points of 57.5%Bi-25.2%In-17.3%Sn and 54.0%Bi-29.7%In-16.3%Sn, a range of ±2%Bi, ±1%In, and ±1%Sn is excluded.

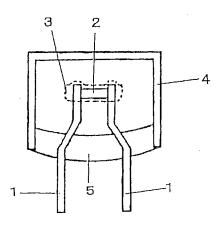
[selective Figure] None



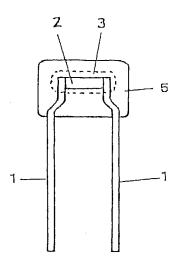




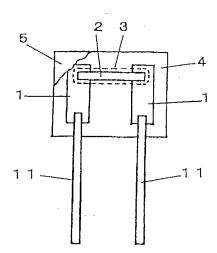




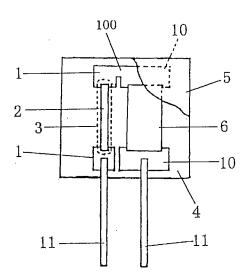
[Fig. 5]



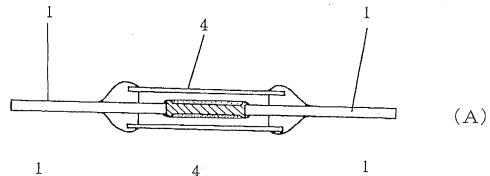
[Fig. 6]

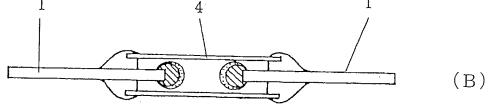


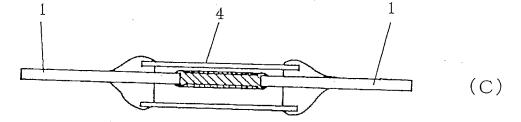
[Fig. 7]

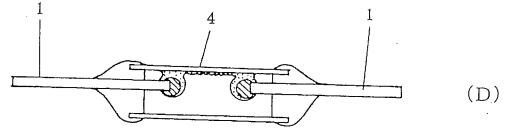


[Fig. 8]

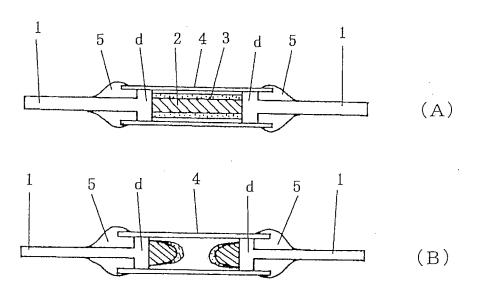








## [Fig. 9]



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